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F. I. Vilesov, B. L. Kurbatov, and Academician A. N. Terenin

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Abstract

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Energy Distribution of Electrons upon Photoionization of Aromatic Amines in the Gas Phase

In recent work on the external photoelectric effect from the surface of solid layers of organic dyes, carried out in our laboratory[^1], it was established that the kinetic energy of the predominant part of the photoelectrons is small (not more than 1 eV) and in most cases does not increase with increasing quantum energy of the incident radiation. This was preliminarily explained by excitation of the positive ion, formed upon photodetachment of the electron, to electronic and vibrational levels. In contrast to the mechanisms of the external photoelectric effect from the surface of metals and semiconductors that are generally accepted at present[^2], it was assumed that in molecular crystals, such as the solid dye layers investigated, the principal part of the photon energy loss occurs in the molecule itself, and not during the motion of the photoelectrons inside the crystal or through excitation of excitons.

To clarify the validity of this hypothesis, in the present work a study was made of the distribution of electrons by kinetic energy upon photoionization of benzene, aniline, methylaniline, and dimethylaniline in the gas phase at pressures of $5 \cdot 10^{-3}$–10^{-3} mm Hg. In addition, the data obtained provide information on the distribution of the excess photon energy above the adiabatic ionization potential of the molecule between the electron and the positive ion formed upon photoionization, information that cannot be obtained by other methods currently in use.

The distribution of photoionization electrons by kinetic energy was studied by the retarding-field method in a cylindrical condenser, the scheme of which is shown in Fig. 1. Vacuum ultraviolet radiation, obtained with the aid of a vacuum monochromator[^3], passes along the axis of a thick-walled inner cylinder made of copper and covered on the outside with a copper electrolytic mesh. To increase the light intensity, the entrance and exit slits of the monochromator were substantially widened, so that the monochromaticity of the radiation was 15 Å. The inner cylinder is milled along radii perpendicular to the axis with a 0.5 mm cutter; the slots limit the angular spread of the electron velocities relative to the axis of the instrument to within ±10°. The middle electrode is a cylinder made of copper electrolytic mesh stretched over copper holders. A constant voltage of +5 V relative to ground is applied to it; this voltage serves to separate the electron and ion currents. The collector is the outer copper cylinder. The

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Fig. 2. Distribution of electrons by kinetic energies in the photoionization of benzene. The curves are reduced to the same light intensity.

Figure 2: Fig. 2. Distribution of electrons by kinetic energies in the photoionization of benzene. The curves are reduced to the same light intensity.

electron current in our experiments was 10^{-13}–10^{-12} A and was measured with an EMU-3 amplifier. Current-voltage characteristics were recorded by varying the voltage on the inner electrode within the limits $-5 \div +5$ V in steps of 0.1 or 0.05 V. If the sign of the potential on the middle electrode is changed, retardation curves for positive ions can be recorded. In form, these curves coincide completely for all the compounds investigated at all ener-

photons. With a retarding potential equal to 0.15 eV, the current decreases to zero. On the basis of these data we consider that the resolving power of the instrument is no worse than 0.2 V. To reduce the influence of the "memory" effect of the instrument, the work was carried out in a gas flow; the pressure was monitored with a Pirani-type thermal manometer.

Fig. 1. Schematic of a cylindrical capacitor for studying the distribution of electrons by kinetic energies in the photoionization of gases and vapors. **1** –window coated with a layer of sodium salicylate; **2** –inner thick-walled cylinder with slits, covered with an electrolytic mesh; **3** –fluoroplast-4 insulators; **4** –middle cylinder made of electrolytic mesh, 30 lines/mm; **5** –collector; **6** –lithium fluoride window; **7** –diaphragm; **8** –shutter for closing the exit slit; **9** –exit slit of the monochromator.

The light intensity was measured with the aid of a fluorescent screen made of sodium salicylate and an FEU-19 photomultiplier. By simultaneously measuring the intensity of the incident light flux and the photoionization current without a retarding field, one can obtain relative photoionization cross sections as a function of the energy of the ionizing photons.

Fig. 2. Distribution of electrons by kinetic energies in the photoionization of benzene. The curves are reduced to the same light intensity.

In Figs. 2 and 3 are presented the curves of the energy distribution of electrons obtained in the photoionization of benzene and methylaniline, -

reduced to the same light intensity. The electron energy distributions for aniline and dimethylaniline qualitatively show a great similarity to the corresponding curves for methylaniline. When the difference between the energy of the ionizing photons and the ionization potential of the molecule of the substance under

Fig. 3. Electron distribution by kinetic energies during photoionization of methylaniline. The curves are reduced to the same light intensity

Figure 3: Fig. 3. Electron distribution by kinetic energies during photoionization of methylaniline. The curves are reduced to the same light intensity

study is small, only one maximum is observed on the electron energy distribution curves; as the quantum energy increases, this maximum shifts toward higher energies. With a further increase in photon energy in the low-energy region, new maxima appear, which, as the quantum energy increases, also shift toward higher energies. In the case of benzene, the appearance of the first group of slow electrons is observed when the photon energy exceeds the ionization potential by 1.5 ± 0.1 eV. For aniline, methylaniline, and dimethylaniline, the corresponding group of electrons appears when the photon energy excess is 1.2, 1.2, and 1.1 eV, respectively. With a further increase in photon energy, for the latter three compounds the appearance of a third group of electrons is observed at photon energies exceeding the ionization potentials by 2.4, 2.3, and 2.2 eV, respectively. For dimethylaniline, in the spectral region studied, a fourth group of electrons appears when the quantum energy is greater than the ionization potential by 2.8 eV.

Fig. 3. Electron distribution by kinetic energies during photoionization of methylaniline. The curves are reduced to the same light intensity.

The interpretation of data on the distribution of electrons by kinetic energies is less complex than in the external photoelectric effect; however, there are several processes that may cause the appearance of new groups of electrons as the energy of the incident radiation increases. Such processes are: (a) ionization with excitation of the molecular ion to electronic and vibrational levels; (b) dissociative ionization according to one of the schemes: $AB + h\nu \rightarrow A^{+} + B + e$ or $AB + h\nu \rightarrow A^{+} + B^{-}$; (c) ejection of more strongly bound electrons. Although at present we do not have data on the positions of the electronic levels of isolated ions of aromatic compounds and cannot give a detailed explanation of the results obtained, certain considerations should be taken into account when considering the processes indicated. In a mass-spectrometric study of the products formed under the action of the full light of a hydrogen lamp[4] on aromatic amines, no fragment ions were detected. The extremely small kinetic energy of the positive ions at all quantum energies likewise indicates the absence of dissociative ionization, since upon dissociation molecular fragments, as a rule, acquire considerable kinetic energies. In benzene and in aromatic amines the first ionization potential is due to the removal of one of the π-electrons of the benzene ring[5]; the σ-electrons of the benzene ring and the p-electrons of the nitrogen atom that do not participate in chemical bonds have ionization potentials greater than 11 eV and, consequently, cannot give rise to groups of slow electrons. These considerations make it possible to conclude that the first of the three mechanisms mentioned is the most probable.

On the curves of the dependence of the effective photoionization cross section on wavelength, a rise is observed at a quantum energy corresponding to the appearance of the group of slow electrons. In most cases this rise is very gradual and small in magnitude, whereas the shape of the electron energy distribution curve changes very sharply. Thus, the method used in the present work makes it possible to obtain a number of new data characterizing the elementary act of photoionization of a free molecule.

The data obtained confirm the assumption that ions produced in the photoeffect from dye films are excited to the upper electronic levels.

Leningrad State University
named after A. A. Zhdanov

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